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Journal Name

ARTICLE

Design and preparation of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) as a novel nanosized ionic liquid catalyst: Application to the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthols

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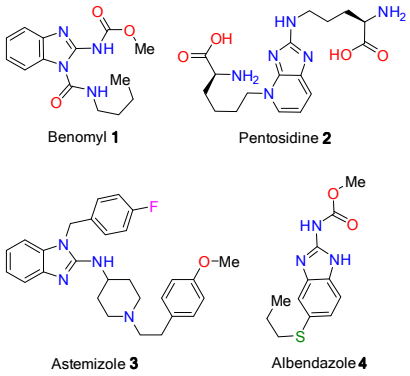
In this work, the novel bifunctional nanosized ionic liquid catalyst [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) was designed synthesized and characterized by using FT-IR, ^{1}H and ^{13}C NMR, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), thermogravimetry (TG), derivative thermogravimetry (DTG) analysis, differential thermal analysis (DTA), and HPLC-mass spectroscopy. The synthesized nanosized catalyst was successfully applied to the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives *via* a straightforward one-pot three component condensation reaction of 2-aminobenzimidazole, 2-naphthol, and a wide range of aromatic aldehydes under mild and solvent-free conditions.

Introduction

Benzimidazole derivatives are interesting heterocyclic compounds which are present in a wide variety of biologically active natural products [1-3]. Some important benzimidazole-derivatives such as, omeprazole, timoprazole, DMA, telmisartan, rabeprazole, and thiabendazole [4,5] have been recently shown as important and renowned marketed drugs with antibacterial and anthelminthic activities, among others. Furthermore, benzimidazole derivatives can interact with DNA, which converts them in versatile drugs targeting DNA and DNA associated processes [6]. Other interesting applications of benzimidazoles include their used as ionic liquids [7] and N-heterocyclic carbine precursors [8,9].

Guanidine-containing organic compounds such as 2-aminobenzimidazole [10,11] present a wide spectrum of applications in the field of pharmaceutical and biological drug design, being the activity against multidrug resistant bacteria the most notable example (Scheme 1) [12-15]. More recently, chiral 2-aminobenzimidazoles have been successfully used as bifunctional Brønsted base/hydrogen bonding organocatalysts [16-20].



Scheme 1: Some therapeutic agents containing 2-aminobenzimidazole moiety

In the last two decades, ionic liquids have played crucial roles in different fields of science emerging as an interdisciplinary area to tackle controversial scientific issues [7,21,22]. Moreover, due to the compliance with green chemistry fundamentals [23] as well as the versatility of ionic liquids as solvents, catalysts, and reagents for different synthetic and industrial applications, the synthesis, chemistry and capabilities of these materials have been well investigated and reported in the literature [24-29]. Despite the advantages of ionic liquid systems in the development of green and sustainable methodologies, many of these materials have been recently found to be toxic towards cells and living organisms [30,31]. Therefore, the synthesis of new and green task-specific molten salts with nanosized morphology could address the above

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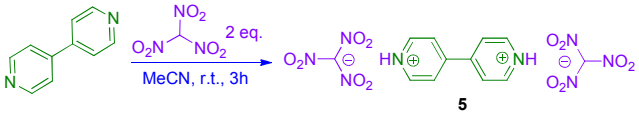
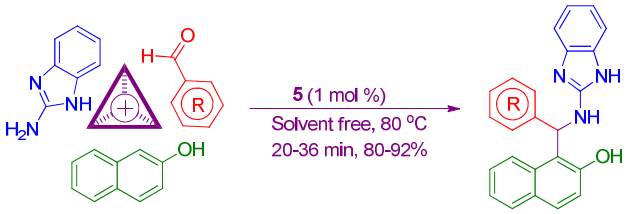
mentioned demerits and open a new vista towards ionic liquids future.

Due to the widespread benefits of one-pot multicomponent processes in the fields of drug discovery, natural product production, library generation, diversity-oriented synthesis (DOS), and combinatorial chemistry, this versatile synthetic tool has persuaded both methodological and synthetic chemists to use it for the preparation of biological pharmacophores under eco-friendly conditions [32-37].

In the present paper, following of our continuous studies on the knowledge-based improvement of magnetically supported ionic liquids and nanosized molten salts as efficient catalysts for the construction of pharmaceutical active molecules [38-46], we present the design and preparation of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM, **5**) as a nanosized ionic liquid catalyst able to promote the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives in a green and simple environmentally gentle manner (Schemes 2 and 3).



Scheme 2: Construction of nanosized ionic liquid catalyst **5**



Scheme 3: Synthesis of target molecules **6a-o** promoted by nanocatalyst **5**

Result and discussion

The general method for the synthesis of the nanosize ionic liquid catalyst **5** is shown in scheme 2, adapted from our previous studies [45,46]. In the present method, to an acetonitrile solution of 4,4'-bipyridine, 2 equivalents of trinitromethane were added. The [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) **5** particles thus obtained were easily isolated and purified by filtration and subsequent washings with MeCN.

To ensure construction of the novel nano ionic liquid **5** as a bifunctional catalyst, this material was analyzed using different techniques such as, FT-IR, ^{1}H and ^{13}C NMR, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and HPLC-mass spectrometry. All the investigated technical skills were synergistic and verified the synthesis of BPDTNM.

The FT-IR spectrum of the prepared nano ionic liquid catalyst **5** was investigated and compared with the starting materials trinitromethane and 4,4'-bipyridine (Figure 1). The broad peak at 3451 cm^{-1} can be used as a proof for distinguishing the -NH stretching vibration mode within the structure. On the other hand, the absorption band at 2934 cm^{-1}, corresponding to the stretching vibration of the aliphatic C-H bond in trinitromethanide (Figure 1a), is completely absent in the spectrum of **5** (Figure1c). As illustrated in the FT-IR spectra (Figures 1a and 1b), all the characteristic absorption bands of the different functional groups [υ C=C (1595 cm^{-1}), υ =C-H (3034 cm^{-1}), and $\upsilon_{as}/\upsilon_{s}$ NO_2 (1625, 1468 cm^{-1})] can be identified in Figure 1c generally showing redshifts in catalyst **5**.

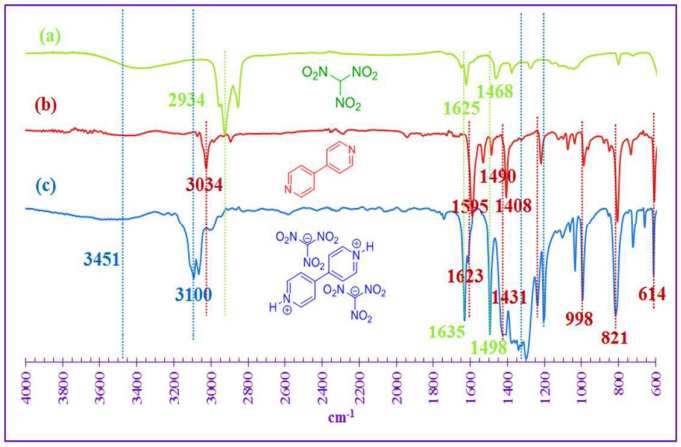


Figure 1: FT-IR spectrum of a) trinitromethane, b) 4,4'-bipyridine, and c) catalyst **5**.

As portrayed in Figure 2, the ^{1}H- and ^{13}CNMR spectra (DMSO-d_6) of **5**, verified the formation of the catalyst. In the ^{1}H NMR spectrum, the aromatic protons of the 4,4'-bipyridine rings, resonate as two multiplets in the aromatic region. The existence of –NH pyridinium groups within the structure of the nanosized catalyst was confirmed by observation of corresponding broad singlet at 12.5 ppm (Figure 2a). With respect to the ^{13}CNMR spectrum, the resonance peak at 160.9 ppm is ascribed to the trinitromethanide carbon, while aromatic carbon atoms appear at 125.8, 122.6, and 119.4 ppm (Figure 2b).

An insight into catalyst **5** was also performed using crystal structure determination by X-ray diffraction (XRD) analysis (Figure 3). From this study, it can be deduced that **5** has a crystalline nature appearing the related diffraction lines at 2ϑ = 19.80°, 20.60°, 24.70°, 26.30°, 28.30°, 29.40°, and 31.20°. Furthermore, the average crystalline size D (nm) of **5** could be estimated according to the

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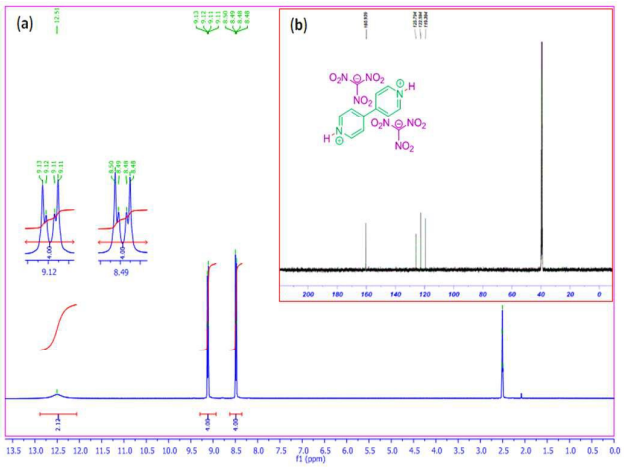

Figure 2: ^{1}HNMR (a) and ^{13}CNMR (b) spectrum of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) **5**

Scherrer equation $D = K\lambda/(\beta \cos\theta)$, where λ is the X-ray wavelength of Cu k_α (1.54Å), K is the Scherrer constant with a value of 0.9, β is the peak width at half maximum (FWHM) of the peak in radians, and θ is the Bragg diffraction angle. The XRD information, including the 2θ value, peak width, particle size, and interplanar distance, is reported in Table 1. According to the Scherrer formula, catalyst **5** particle size is estimated to be between 15 and 33 nm.

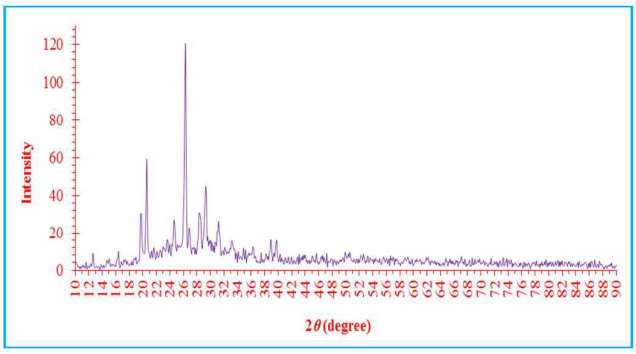

Figure 3: XRD pattern of catalyst

Table 1: XRD data for **5**.

Entry	2ϑ	Peak width [FWHM] (degree)	Size [nm]	Interplanar distance [nm]
1	19.80	0.32	25.21	0.447859
2	20.60	0.24	33.65	0.430643
3	24.70	0.48	16.95	0.360011
4	26.30	0.30	27.20	0.338460
5	28.30	0.55	14.90	0.314978
6	29.40	0.45	18.25	0.303439
7	31.20	0.53	15.53	0.295580

Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) are two helpful techniques which provide valuable information about particle size and morphology of materials. Figure 4 shows the SEM and HRTEM images of catalyst **5** crystals, where lattice fringes with three different inter-planar distances of 0.43, 0.33, and 0.30 nm corresponding to contrast profiles of the 2ϑ = 20.60, 26.30, 29.40 degree diffraction lines are clearly revealed (Figure 4a-c). Also, according to the obtained SEM and HRTEM micrographs, the nano-catalyst particle size was determined to be between 33.6 and 60.1 nm, which is in accordance with the extracted information from the XRD analysis.

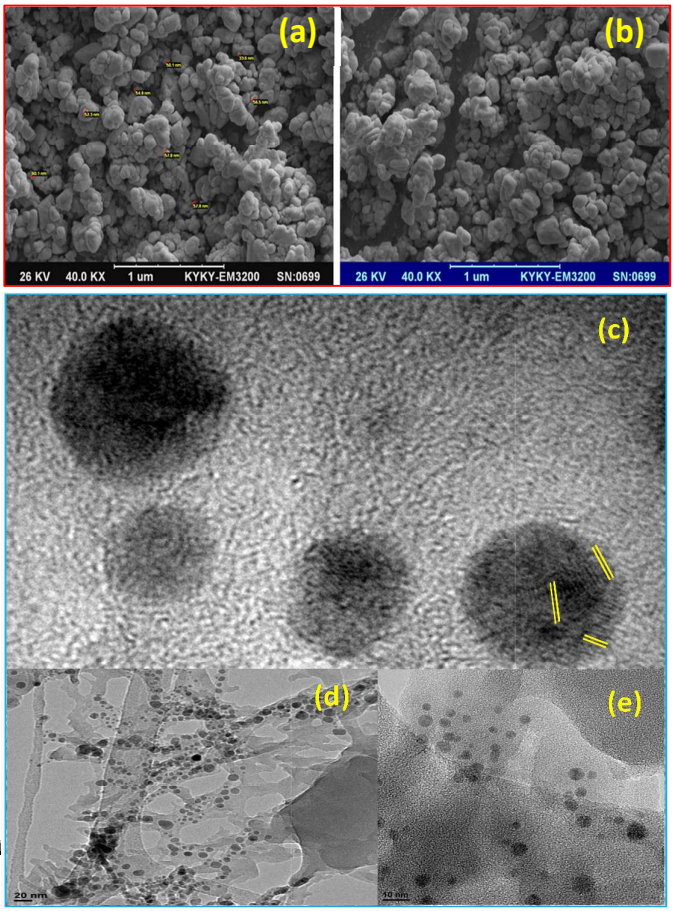

Figure 4: SEM (a-b) and HRTEM (c-e) micrographs of **5**

In order to monitor the thermal stability and behavior of the [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM), the thermogravimetric analysis (TGA), differential thermal analysis

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(DTA), and differential thermogravimetry (DTG) were conducted (Figure 5). As depicted, the main weight loss and decomposition of the target catalyst took place around 200-250 °C in a single exothermic step, indicating a good thermal stability (up to 200 °C) of **5** which and enabling its use at elevated temperatures.

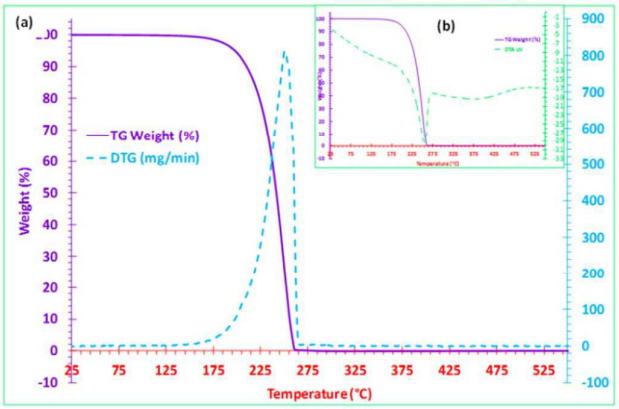


Figure 5: Thermal stability studies of **5**: (a) thermogravimetric analysis and differential thermogravimetry (TGA/DTG). (b) thermogravimetric analysis and differential thermal analysis (TGA/DTA).

Catalyst **5** was also analyzed by HPLC–electrospray mass spectrometry. As depicted in Figure 6a for the positive mode, under the analysis conditions, we only detected a peak at m/z = 157, corresponding to the [4,4'-bipyridin]-1-ium moiety. When analyzing the negative mass spectrum (Figure 6b), and due to the aqueous instability of the trinitromethanide carbanion, different identified [(226: $^{-}C(OH)(NO_2)_2CH(NO_2)_2$; 209: $^{-}C(NO_2)_2CH(NO_2)_2$] and non-identified polynitro coupled species were detected [47].

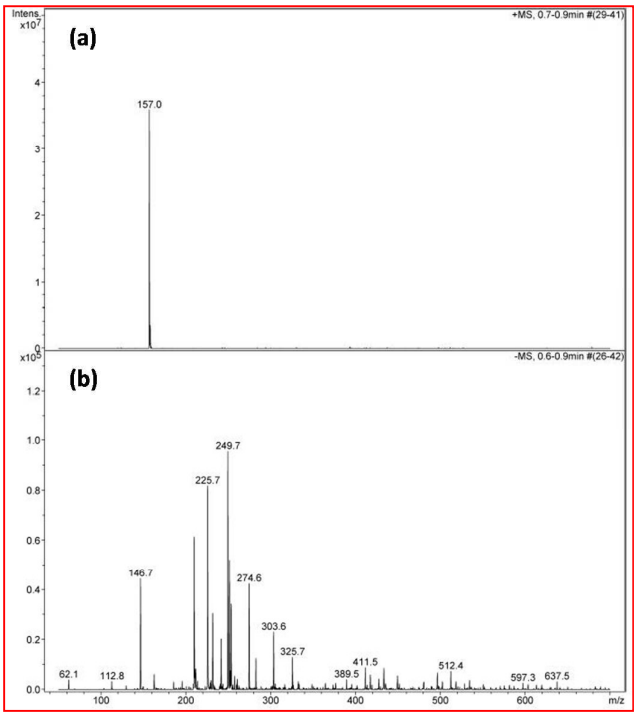
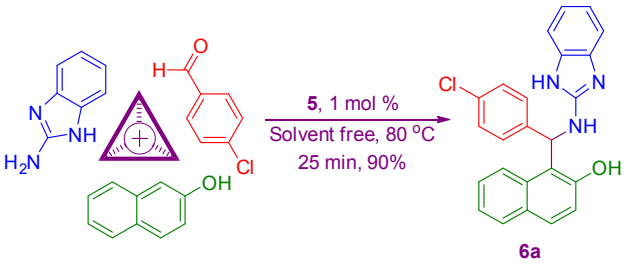


Figure 6: a) Low-resolution positive mode HPLC–electrospray mass spectrum of catalyst **5**. b) Low-resolution negative mode HPLC–electrospray mass spectrum of catalyst **5**.

After the structural analysis of the prepared nano ionic liquid **5**, we proved its catalytic activity in the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives *via* a one-pot condensation reaction between aromatic aldehydes, 2-aminobenzimidazole and 2-naphthol. Initially, to evaluate the effect on the yield of the different reaction conditions involved in the process, we studied the condensation reaction of 4-chlorobenzaldehyde, 2-aminobenzimidazole, and 2-naphthol (Scheme 4). After a careful screening of temperatures, catalyst loadings, and solvents (Table 2), the optimized reaction conditions for the synthesis of 1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(4-chlorophenyl)methyl)naphthalen-2-ol (**6a**) involved the use of 1 mol% of **5** at 80 °C under neat conditions (Table 2, entry 1).



Scheme 4: Model reaction for the evaluation of the reaction conditions.

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Journal Name

ARTICLE

Table 2: Optimization of reaction conditions for the synthesis of molecule **6a**.[1]

Entry	Solvent	Catalyst loading (mol%)	Temperature (°C)	Time (min)	Yield (%)[2]
1	**-**	**1**	**80**	**25**	**90**
2	-	1	60	40	80
3	-	1	100	20	90
4	-	-	80	60	40
5	-	0.5	80	35	78
6	-	1.5	80	25	91
7	Water	1	80	60	15
8	Ethanol	1	reflux	60	-
9	Acetonitrile	1	reflux	70	-
10	Ethyl acetate	1	reflux	70	-
11	*n*-Hexane	1	reflux	50	20

[1] Reaction conditions: 4-chlorobenzaldehyde (1 mmol, 0.140 g), 2-aminobenzimidazole (1 mmol, 0.133 g), 2-naphthol (1 mmol, 0.144 g). [2] Isolated yield.

Also, at the optimal reaction conditions for the model test (1 mol% of catalyst, 80 °C under solvent free conditions, Scheme 4) in a comparative mode, the catalytic performance of the novel nanosized ionic liquid catalyst **5** and three ionic liquids with trinitromethan anion including {[1,4-DHPyrazine][$C(NO_2)_3]_2$}, {[HMIM] $C(NO_2)_3$} and {[2,6-DMPyH]$C(NO_2)_3$} were investigated. The achieved data indicated that the novel ionic liquid **5** performs better than other catalysts and gives better experimental results (Table 3).

To demonstrate the scope and efficiency of the optimized nanocatalyzed construction of 1-functionalized 2-naphthols **6**, a wide series of aromatic aldehydes, including electron-donating and electron-withdrawing substituents, were submitted to the one-pot reaction with 2-aminobenzimidazole and 2-naphthol. As depicted in Table 4, irrespective of the electronic nature of the aromatic aldehyde, all the tested reactions afforded the target compounds in short times with high to excellent yields. Interestingly, this methodology could be also applied to terephthalaldehyde, electrophile which afforded the sterically crowded compound **6n** in a 90% yield after 30 min (Table 4, entry 14).

Table 3: Screening of the catalysts with trinitromethan anion for the synthesis of compound **6a**

Entry	Applied catalyst	Time (min.)	Yield (%)	Ref.
1	{[1,4-DHPyrazine][$C(NO_2)_3]_2$}	30	85	46a
2	{[HMIM]$C(NO_2)_3$}	40	80	46b
3	{[2,6-DMPyH]$C(NO_2)_3$}	30	83	46c
4	Novel ionic liquid catalyst **5**	25	90	-

Table 4: **5**-catalyzed synthesis of products **6a-o** under solvent free conditions at 80 °C.[1]

Entry	R	Time (min)	Structure	**Product**	Yield (%)[2]	M.p. (°C)

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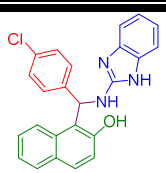
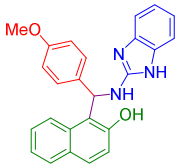
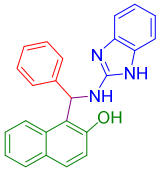
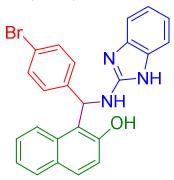
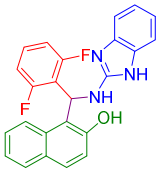
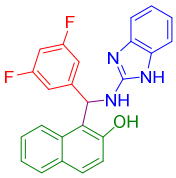
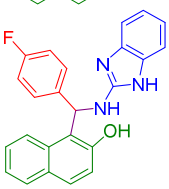
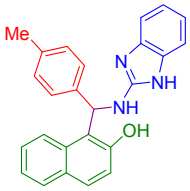
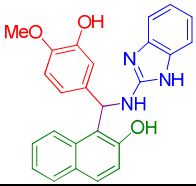
1	4-Cl	25		**6a**	90	195-197
2	4-MeO	28		**6b**	90	171-173
3	H	25		**6c**	89	195-196
4	4-Br	20		**6d**	90	199-201
5	2,6-F_2	20		**6e**	89	152-154
6	3,5-F_2	20		**6f**	92	207-209
7	4-F	25		**6g**	88	195-196
8	4-Me	30		**6h**	87	182-184
9	3-OH-4-Me	30		**6i**	85	166-168

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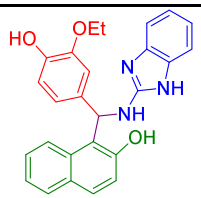
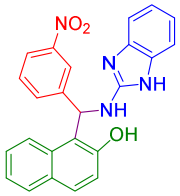
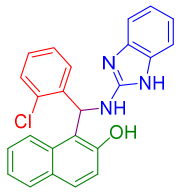
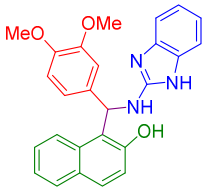
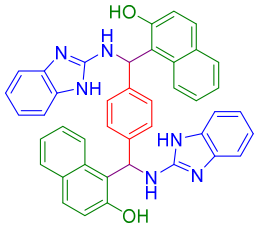
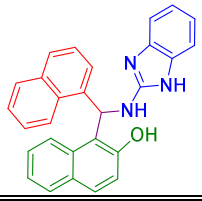
10	3-EtO-4-OH	35		**6j**	80	182-184
11	3-NO_2	25		**6k**	90	197-198
12	2-Cl	24		**6l**	89	144-146
13	3,4-$(MeO)_2$	36		**6m**	83	187-190
14	Terephthalaldehyde	30		**6n**	90	206-208
15	1-naphthaldehyde	30		**6o**	85	149-151

[1]Reaction conditions: arylaldehydes (1 mmol), 2-aminobenzimidazole (1 mmol, 0.133 g), 2-naphthol (1 mmol, 0.144 g).
[2]Isolated yield.

A plausible mechanistic route of the **5**-catalyzed synthesis of compounds **6** is presented in Scheme 5. We suggest that in the presence of catalyst **5**, the activated aryl aldehydes undergo nucleophilic attack from 2-naphtol to generate the related Knoevenagel adduct **A**. Then, this activated electrophile suffers Michael addition from 2-aminobenzimidazole to afford intermediate **B**, which after a proton transfer process generates the final product **6**.

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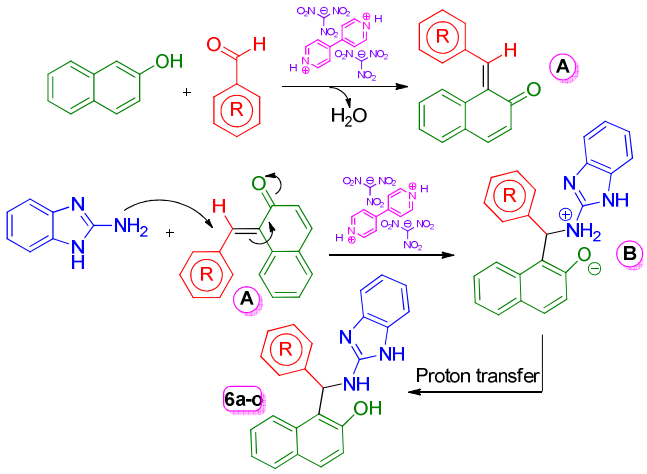

Scheme 5: Plausible mechanistic route towards the synthesis of target compounds **6**.

Conclusion

In summary, a new bifunctional nanosized ionic liquid catalyst, [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM, **5**), has been designed, synthesized, and fully characterized by FT-IR, ^{1}H and ^{13}C NMR, XRD, SEM, HRTEM, TG, DTG, DTA, and HPLC-mass spectrometry analyses. The constructed nanosized catalyst has been successfully applied for the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives. The main merits of the present method are the robustness and high activity of the catalyst, the benign neat reaction conditions, an easy work-up and clean reaction profile, and the short reaction times with excellent yields.

Experimental

2.1.General information.

All chemicals and solvents were of reagent grade and purchased from Sigma-Aldrich, Fluka, Merck, and Across Organic Chemical Companies. All reagents were used without any further purification. Solvents were dried, distilled and stored over molecular sieves. TLC was performed on UV-active aluminium-backed silica gel plates F254 plates. Melting points were measured with a Thermo Scientific apparatus and are uncorrected. Fourier transform-infrared spectra (FT-IR) of the samples were recorded on a Perkin–Elmer FT-IR spectrometer 17259 using KBr disks. ^{1}H NMR (300 MHz and 400 MHz) spectra were obtained on a Bruker Avance 300 NMR and a Bruker Avance 400 NMR spectrometers, respectively, under proton coupled mode using deuterated DMSO as a solvent. ^{13}C NMR (101 MHz) spectra were acquired on a Bruker Avance 400 NMR spectrometer in the proton decoupled mode at 20 °C in deuterated DMSO as solvent, unless otherwise stated. Chemical shifts are given in δ (parts per million) and the coupling constants (*J*) in hertz. ^{19}F NMR (282 MHz) spectra were recorded on a Bruker Avance 300 NMR spectrometer, in proton coupled mode. Data for ^{1}HNMR spectra is reported as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad), coupling constant (Hz), and integration. Thermogravimetric analyses (TGA) were carried out on Perkin–Elmer TGA under nitrogen atmosphere at 25°C and using a heating rate of 10 °C min^{-1} up to 550 °C. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOLJEM-2010 microscope operating with an accelerating voltage of 200 kv. Sample was prepared by drop casting the dispersed particles onto a 200-mesh copper grid coated with a holey carbon film. Scanning electron microscopy (SEM) studies were performed using a TESCAN/MIRA with a maximum acceleration voltage of the primary electrons between 10 and 15 kV. X-ray diffraction (XRD) analysis was performed using a Bruker D8-Advance apparatus equipped with a monochromatized Cu Kα (λ= 0.154nm) X-ray source in the range $2° < 2\vartheta < 90°$. Low resolution mass spectra (EI, 70 eV) were obtained using an Agilent 5973 Network spectrometer, with fragment ions m/z reported with relative intensities (%) in parentheses. Electrospray ionization low-resolution HPLC mass spectra were recorded on an Agilent 1100 series apparatus.

General procedure for the synthesis of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) (5) as a nanosized ionic liquid catalyst (Scheme 2).

To a round bottom flask containing 4,4'-bipyridine (5 mmol, 0.780 g) dissolved in acetonitrile (15 mL), trinitromethane (10 mmol, 1.51 g) was portion-wise added under vigorous stirring at room temperature. A light yellow powder was quickly formed and the stirring was continued for three hours. Then, the obtained powder was collected by filtration, washed with acetonitrile (3 × 5 mL) and air-dried. All spectral data confirmed the formation of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM, **5**).

General procedure for the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives 6 using [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM, 5) as a catalyst (Scheme 3).

In a round bottom flask, to a mixture of the corresponding aromatic aldehyde (1 mmol), 2-naphtol (1 mmol, 0.144 g), and 2-aminobenzimidazole (1 mmol, 0.133 g), [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) **5** (1 mol%, 0.0046 g) was added. Then, the reaction mixture was stirred at 80 °C for the corresponding time, as indexed in Table 3, under neat conditions. The progress of the reaction was checked by TLC (*n*-hexane/EtOAc). Once demonstrated full conversion, the reaction was quenched at room temperature. Purification of the obtained products by crystallization in hot EtOH afforded pure compounds **6**, which were dried at 100 °C in an oven.

Spectral data

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[4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) (5):
Isolated as a light yellow solid, Melting point: 94 – 96 °C; ^{1}HNMR (300 MHz) δ 12.51 (br. s, 2H), 9.12 (m, 4H), 8.49 (m, 4H); ^{13}CNMR (101 MHz) δ 160.9, 125.8, 122.6, 119.4; m/z (HPLC/+MS-ESI): 157 [(4,4'-bipyridin)-1-ium].

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(4-chlorophenyl)methyl)naphthalen-2-ol (6a):
Isolated as white solid, (359 mg, 90%), Melting point: 195 – 197 °C; FT-IR (KBr): υ (cm^{-1}) = 3419, 3377, 3061, 1627, 1606, 1583, 1466, 1266, 740; ^{1}HNMR (400 MHz) δ 10.72 (br. s, 1H), 10.59 (br. s, 1H), 7.98 (br. s, 1H), 7.83 (d, *J* = 7.9, 1H), 7.79 (d, *J* = 8.9, 1H), 7.45 (br. s, 2H), 7.34 – 7.22 (m, 6H), 7.17 (d, *J* = 8.5, 2H), 7.13 (d, *J* = 8.0, 1H), 6.69 (br. s, 2H); ^{13}C NMR (101 MHz) δ 155.2, 153.1, 142.5, 131.9, 130.6, 129.5, 128.7, 128.5, 127.9, 127.8, 126.6, 122.6, 120.1, 119.4, 118.8, 114.8, 108.9, 51.4; MS (EI) m/z (%): 254 (100), 144 (24), 133(9), 115 (12).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(4-methoxyphenyl)methyl)naphthalen-2-ol (6b):
Isolated as white solid, (355 mg, 90%), Melting point: 171 – 173 °C; FT-IR (KBr): υ (cm^{-1}) = 3398, 3053, 2951, 1627, 1606, 1585, 1508, 1466, 1437, 1266, 1175, 741; ^{1}H NMR (300 MHz) δ 10.76 (br. s, 2H), 8.01 (br. s, 1H), 7.82 (d, *J* = 8.0, 1H), 7.77 (d, *J* = 8.9, 1H), 7.45 (br. s, 2H), 7.34 – 7.13 (m, 6H), 7.08 (d, *J* = 8.5, 1H), 6.88 (br. s, 2H), 6.82 (d, *J* = 8.5, 2H), 3.68 (s, 3H); ^{13}C NMR (101 MHz) δ 158.2, 155.9, 153.6, 135.5, 132.5, 129.6, 129.1, 127.6, 126.9, 123.6, 123.0, 120.5, 119.5, 119.2, 115.3, 113.9, 109.3, 55.4, 52.0; MS (EI) m/z (%): 250 (100), 207 (12), 144 (21), 133 (10), 115 (10).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(phenyl)methyl)naphthalen-2-ol (6c):
Isolated as white solid, (325 mg, 89%), Melting point: 195 – 196 °C; FT-IR (KBr): υ (cm^{-1}) = 3405, 3380, 3058, 1634, 1608, 1587, 1506, 1468, 1267, 1051, 747, 699, 522; ^{1}H NMR (300 MHz) δ 10.77 (br. s, 2H), 8.02 (br. s, 1H), 7.83 (d, *J* = 7.9, 1H), 7.79 (d, *J* = 8.9, 1H), 7.57 – 7.36 (m, 2H), 7.35 – 7.20 (m, 6H), 7.20 – 7.11 (m, 4H), 6.94 – 6.83 (m, 2H); ^{13}C NMR (101 MHz) δ 155.9, 153.7, 143.7, 132.6, 129.7, 129.1, 128.8, 128.5, 126.9, 126.6, 126.4, 123.7, 123.0, 120.4, 119.9, 119.8, 119.5, 52.4; MS (EI) m/z (%): 220 (26), 144 (100), 133 (10), 115 (46), 84 (38), 63 (42).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(4-bromophenyl)methyl)naphthalen-2-ol (6d):
Isolated as white solid, (398 mg, 90%), Melting point: 199 – 201 °C; FT-IR (KBr): υ (cm^{-1}) = 3418, 3374, 3055, 1626, 1605, 1583, 1516, 1465, 1357, 1266, 1070, 1010, 848, 742; ^{1}H NMR (300 MHz) δ 10.72 (br. s, 2H), 7.99 (br. s, 1H), 7.84 (d, *J* = 7.9, 1H), 7.80 (d, *J* = 8.9, 1H), 7.46 (d, *J* = 8.5, 4H), 7.35 – 7.03 (m, 7H), 6.96 – 6.83 (m, 2H); ^{13}C NMR (101 MHz) δ 155.7, 153.7, 143.4, 132.5, 131.3, 130.0, 129.2, 129.0, 128.7, 127.1, 123.5, 123.1, 120.0, 119.9, 119.6, 119.3,112.6, 52.0; MS (EI) m/z (%): 300 (9), 298 (9), 144 (100), 133 (8), 115 (46), 84 (12), 78 (30), 66 (14), 63 (35).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(2,6-difluorophenyl)methyl)naphthalen-2-ol (6e):
Isolated as white solid, (356 mg, 89%), Melting point: 152 – 154 °C; FT-IR (KBr): υ (cm^{-1}) = 3423, 3388, 3061, 2975, 1633, 1603, 1579, 1511, 1465, 1308, 1264, 1046, 989, 746; ^{1}H NMR (300 MHz) δ 10.73 (br. s, 1H), 10.31 (br. s, 1H), 8.27 (d, *J* = 8.5, 1H), 7.82 (d, *J* = 8.0, 1H), 7.77 (d, *J* = 8.9, 1H), 7.55 – 7.49 (m, 1H), 7.41 – 7.32 (m, 1H), 7.33 – 7.08 (m, 6H), 6.98 – 6.83 (m, 4H); ^{13}C NMR (101 MHz) δ, 161.4 (dd, *J* = 247.3, 8.0), 155.1, 154.0, 143.6, 133.9, 132.3, 130.1, 129.0 – 128.6 (m), 127.1, 122.9, 122.7, 120.5, 119.3 – 119.0 (m), 118.5, 115.5, 112.2 - 111.9 (m), 109.4, 56.5; ^{19}F NMR (282 MHz) δ -110.19; MS (EI) m/z (%): 257 (10), 238 (39), 144 (100), 133 (15), 115 (46).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(3,5-difluorophenyl)methyl)naphthalen-2-ol (6f):
Isolated as white solid, (369 mg, 92%), Melting point: 207 – 209 °C; FT-IR (KBr): υ (cm^{-1}) = 3409, 3089, 3055, 1626, 1605, 1577, 1519, 1466, 1304, 1271, 1116, 983, 848, 819, 738, 536, 430; ^{1}H NMR (300 MHz) δ 10.69 (br. s, 2H), 8.00 (br. s, 1H), 7.84 (t, *J* = 8.5, 2H), 7.50 (br. t, *J* = 7.1, 2H), 7.35 – 7.14 (m, 5H), 7.05 (tt, *J* = 9.0, 2.3, 1H), 6.91 (m, 4H); ^{13}C NMR (101 MHz) δ 162.7 (dd, *J* = 246.0, 13.0), 155.6, 153.7, 149.3 (t, *J* = 8.0), 132.4, 130.3, 129.2, 129.0, 127.3, 123.2, 120.1, 119.9, 119.25, 119.18, 115.1, 109.7 – 109.4 (m), 102.2 (t, *J* = 26.0), 52.1; ^{19}F NMR (282 MHz) δ -108.10; MS (EI) m/z (%): 256 (22), 144 (100), 133 (9), 115 (47), 84 (25), 78 (27), 66 (27), 63 (32).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(4-fluorophenyl)methyl)naphthalen-2-ol (6g):
Isolated as white solid, (337 mg, 88%), Melting point: 195 – 196 °C; FT-IR (KBr): υ (cm^{-1}) = 3423, 3382, 3066, 1633, 1608, 1586, 1504, 1467, 1435, 1267, 1053, 854, 736, 579, 504, 436; ^{1}H NMR (300 MHz) δ 10.74 (br. s, 2H), 8.01 (br. s, 1H), 7.88 – 7.74 (m, 2H), 7.58 – 7.37 (m, 2H), 7.36 – 7.21 (m, 4H), 7.20 – 7.04 (m, 5H), 6.95 – 6.84 (m, 2H); ^{13}C NMR (101 MHz) δ 161.2 (d, *J* = 242.0), 155.8, 153.7, 151.0, 139.9, 132.5, 129.9, 129.1, 129.0, 128.3 (d, *J* = 8.0), 127.0, 123.4, 123.0, 121.7, 120.1, 119.9, 119.4, 115.2 (d, *J* = 21.0), 52.0; ^{19}F NMR (282 MHz) δ -115.10; MS (EI) m/z (%): 238 (38), 144 (100), 133 (9), 115 (66), 84 (13), 78 (22), 66 (14), 63 (28).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(*p*-tolyl)methyl)naphthalen-2-ol (6h):
Isolated as white solid, (330 mg, 87%), Melting point: 182 – 184 °C; FT-IR (KBr): υ (cm^{-1}) = 3395, 3374, 3058, 1627, 1605, 1582, 1507, 1467, 1266, 1051, 814, 739, 482; ^{1}H NMR (300 MHz) δ 10.75 (br. s, 2H), 7.99 (br. s, 1H), 7.82 (d, *J* = 7.9, 1H), 7.77 (d, *J* = 8.9, 1H), 7.58 – 7.34 (m, 2H), 7.33 – 7.00 (m, 9H), 6.95 – 6.82 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (101 MHz) δ 155.9, 153.7, 140.6, 135.6, 132.5, 129.8, 129.7, 129.4, 129.0, 126.8, 126.4, 123.6, 122.9, 120.6, 119.9, 119.6, 119.5, 52.2, 21.0; MS (EI) m/z (%):144 (100), 115 (52).

1-(((1H-benzo[d]imidazol-2-yl)amino)(3-hydroxy-4-methoxyphenyl)methyl)naphthalen-2-ol (6i):
Isolated as white solid, (349 mg, 85%), Melting point: 166 – 168 °C; FT-IR (KBr): υ (cm^{-1}) = 3532, 3394, 3049, 1632, 1607, 1586, 1505, 1468, 1264, 1123, 822, 739, 493; ^{1}H NMR (300 MHz) δ 10.74 (br. s, 2H), 8.81 (br. s, 1H), 7.99 (br. s, 1H), 7.82 (d, *J* = 7.9, 1H), 7.77 (d, *J* = 8.9, 1H), 7.43 (br. s, 2H), 7.32 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 7.02 (d, *J* = 8.5, 1H), 6.89 (br. s, 2H), 6.79 (d, *J* = 8.5, 1H), 6.77 – 6.61 (m, 2H), 3.69 (s, 3H); ^{13}C NMR (101 MHz) δ 155.9, 153.7, 146.6, 146.5, 136.2, 132.6, 129.5, 129.0, 126.8, 123.7, 122.9, 120.7, 120.0, 119.6, 119.4, 117.0, 114.2, 112.4, 109.2, 56.1, 52.1; MS (EI) m/z (%):144 (100), 115 (66).

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1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(3-ethoxy-4-hydroxyphenyl)methyl)naphthalen-2-ol (6j**):**
Isolated as pale yellow solid, (340 mg, 80%), Melting point: 182 – 184 °C; FT-IR (KBr): υ (cm^{-1}) = 3517, 3393, 3064, 2975, 1626, 1606, 1584, 1509, 1468, 1434, 1406, 1352, 1267, 1121, 1043, 827, 811, 740, 637, 506, 451; ^{1}H NMR (300 MHz) δ 10.77 (br. s, 1H), 8.76 (br. s, 1H), 8.11 – 7.95 (m, 1H), 7.90 – 7.64 (m, 3H), 7.54 (br. s, 1H), 7.42 (br. s, 1H), 7.33 – 7.06 (m, 5H), 7.05 – 6.86 (m, 3H), 6.78 – 6.54 (m, 2H), 3.94 – 3.70 (m, 2H), 1.21 (t, *J* = 7.8, 7.0, 3H); ^{13}C NMR (101 MHz) δ 155.9, 153.7, 146.7, 146.0, 145.3, 134.6, 134.3, 132.6, 129.6, 129.0, 128.8, 126.2, 124.3, 122.9, 122.5, 121.1, 119.5, 119.4, 115.8, 113.0, 64.4, 52.5, 15.1; MS (EI) m/z (%): 144 (100), 133 (7), 115 (53), 84 (13), 78 (19), 66 (14), 63 (24).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(3-nitrophenyl)methyl)naphthalen-2-ol (6k**):**
Isolated as yellow solid, (369 mg, 90%), Melting point: 197 – 198 °C; FT-IR (KBr): υ (cm^{-1}) = 3365, 3336, 3052, 1634, 1574, 1516, 1465, 1350, 1269, 741, 701, 546; ^{1}H NMR (300 MHz) δ 10.74 (br. s, 1H), 10.63 (br. s, 1H), 8.20 (s, 1H), 8.07 (dd, *J* = 7.8, 1.8, 2H), 7.89 – 7.81 (m, 2H), 7.68 (d, *J* = 7.8, 1H), 7.60 – 7.46 (m, 3H), 7.36 – 7.29 (m, 1H), 7.26 (d, *J* = 8.5, 2H), 7.23 – 7.17 (m, 2H), 6.90 (d, *J* = 4.2, 2H); ^{13}C NMR (101 MHz) δ 155.6, 153.7, 151.0, 148.2, 146.6, 133.4, 132.4, 130.4, 130.1, 129.2, 128.9, 127.4, 123.2, 121.8, 121.7, 120.9, 119.3, 119.2, 115.4, 109.4, 52.0; MS (EI) m/z (%): 276 (11), 265 (100), 230 (28), 219 (49), 202 (16), 193 (14), 144 (54),115 (27).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(2-chlorophenyl)methyl)naphthalen-2-ol (6l**):**
Isolated as white solid, (355 mg, 89%), Melting point: 144 – 146 °C; FT-IR (KBr): υ (cm^{-1}) = 3371, 3058, 1628, 1600, 1568, 1465, 1270, 1043, 743; ^{1}H NMR (300 MHz) δ 10.53 (br. s, 1H), 10.25 (br. s, 1H), 8.13 (d, *J* = 8.5, 1H), 7.83 – 7.73 (m, 3H), 7.48 – 7.37 (m, 2H), 7.36 – 7.22 (m, 4H), 7.22 – 7.12 (m, 4H), 6.94 – 6.80 (m, 2H); ^{13}C NMR (101 MHz) δ 155.1, 154.1, 140.9, 133.0, 132.7, 130.1, 129.9, 129.8, 129.0, 128.8, 128.6, 126.7, 123.3, 122.8, 119.9, 119.6, 119.3, 118.3, 109.1, 51.7; MS (EI) m/z (%):220 (11), 144 (100), 133 (12), 115 (47), 84 (10), 78 (16), 63 (20).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(3,4-dimethoxyphenyl)methyl)naphthalen-2-ol (6m**):**
Isolated as white solid, (352 mg, 83%), Melting point: 187 – 190 °C; FT-IR (KBr): υ (cm^{-1}) = 3393, 3052, 2935, 1632, 1606, 1586, 1506, 1469, 1405, 1353, 1274, 1028, 1002, 822, 754, 742, 655, 522 ; ^{1}H NMR (300 MHz) δ 10.78 (br. s, 2H), 8.03 (br. s, 1H), 7.82 (d, *J* = 7.9, 1H), 7.77 (d, *J* = 8.9, 1H), 7.54 (br. s, 1H), 7.49 – 7.36 (m, 1H), 7.30 (d, *J* = 8.5, 1H), 7.24 (d, *J* = 8.8, 1H), 7.17 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 8.5, 1H), 7.01 (br. s, 1H), 6.89 (br. s, 2H), 6.83 (d, *J* = 8.4, 1H), 6.77 (dd, *J* = 8.5, 1.5, 1H), 3.68 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz) δ 155.9, 153.7, 148.9, 147.9, 143.1, 136.0, 132.6, 129.6, 129.0, 126.8, 123.8, 123.0, 120.6, 119.7, 118.9, 115.1, 112.1, 111.0, 109.4, 55.9, 52.5; MS (EI) m/z (%): 292 (10), 280 (100), 277 (11), 261 (32), 144 (11).

1,1'-(1,4-phenylenebis(((1*H*-benzo[*d*]imidazol-2-yl)amino)methylene))bis(naphthalen-2-ol) (6n**):**
Isolated as yellow solid, (586 mg, 90 %), Melting point: 206 – 208 °C; FT-IR (KBr): υ (cm^{-1}) = 3383, 3058, 1628, 1603, 1572, 1515, 1466, 1358, 1266, 819, 741; ^{1}H NMR (300 MHz) δ 10.72 (br. s, 4H), 7.99 (br. s, 2H), 7.86 – 7.59 (m, 5H), 7.59 – 7.33 (m, 4H), 7.33 – 6.99 (m, 13H), 6.98 – 6.74 (m, 4H); ^{13}C NMR (101 MHz) δ 155.8, 153.6, 141.6, 132.5, 129.6, 129.0, 128.0, 126.5, 126.4, 126.1, 123.1, 122.9, 120.5, 119.5, 119.1, 109.1, 52.2; MS (EI) m/z (%): 144 (100), 115 (55).

1-(((1*H*-benzo[*d*]imidazol-2-yl)amino)(naphthalen-1-yl)methyl)naphthalen-2-ol (6o**):**
Isolated as yellow solid, (353 mg, 85%), Melting point: 149 – 151 °C; FT-IR (KBr): υ (cm^{-1}) = 3373, 3055, 1600, 1627, 1568, 1511, 1464, 1269, 778, 742; ^{1}H NMR (300 MHz) δ 10.64 (br. s, 2H), 8.25 (d, *J* = 8.5, 1H), 8.07 (d, *J* = 8.5, 1H), 7.93 (d, *J* = 8.5, 1H), 7.86 – 7.55 (m, 6H), 7.50 – 7.14 (m, 8H), 6.95 – 6.6.82 (m, 2H); ^{13}C NMR (101 MHz) δ 155.4, 153.8, 138.3, 134.1, 133.1, 131.6, 129.8, 129.1, 128.0, 126.8, 126.6, 126.4, 125.9, 125.6, 125.4, 124.2, 123.4, 123.1, 122.9, 119.5, 119.1, 109.1, 51.4; MS (EI) m/z (%): 270 (10), 144 (100), 133 (13), 115 (47), 63 (10).

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Design and preparation of [4,4'-bipyridine]-1,1'-diium trinitromethanide (BPDTNM) as a novel nanosized ionic liquid catalyst: Application to the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthols

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A novel bifunctional nanosized molten salt catalyst promoted the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives under mild reaction conditions.